

Time-evolution of nanoscale systems by finite difference method

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Abstract. Using finite difference method, time evolution of a typical metal-molecule-metal system is studied by introducing a new method to solve general related Volterra *integro – differentialequation (IDE)*. Discretization in time domain is applied for one dimensional chain tight binding model in several cases by defining a *matrixintegro – differentialequation (MIDE)*. Results are compatible with their analytical counterparts and show more accuracy than other numerical methods like Runge Kutta (RK). Charge transport properties in a trans-polyacetylene chain are found by studying the time evolution of charge density in it and current-voltage diagram is calculated.

Key words: time evolution, green function, molecular junction, finite difference method.

1 Introduction

Recently, Metal-Molecule-Metal (MMM) structures (Figure 1) have attracted scientists. Their vast applications, include electrical, optical, mechanical, *etc* have led scientists to produce devices with new abilities and have improved efficiencies relative to their primary counterparts [1–5]. Well predicting behaviour of MMM systems requires investigating time-evolution of their transport properties. Many efforts have been done to investigate time dependence of transport properties in MMM structures. Generally, Green's function formalism and density functional theory, have extensively applied to study time evolution of MMM structures [6–12]. In the Green's function formalism, transport properties of MMM systems can be deduced by applying Green's function in the energy representation, $G(E)$, which can be calculated as follows:

$$G(E) = [(E + i0^+)I - H - \Sigma(E)]^{-1} \quad (1.1)$$

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In which H , $\Sigma(E)$ and E are Hamiltonian of the molecule and self-energy of the system in energy E , respectively. The Fourier transform of $G(E)$, suggests impulse response ($G(t)$) as:

$$G(t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{\frac{-iEt}{\hbar}} G(E) dE \quad (1.2)$$

which satisfies the Fourier transform of equation (1.1) as follows:

$$(i\hbar \frac{\partial}{\partial t} - H - \Sigma) G(t) = I\delta(t) \quad (1.3)$$

Taking the energy dependence into account, the product of Σ and G becomes a convolution in time domain then equation (1.3) can be rewritten as [13]:

$$(i\hbar \frac{\partial}{\partial t} - H) G(t) - \int \Sigma(t-t') G(t') dt' = I\delta(t) \quad (1.4)$$

Equation (1.4) is a non-homogeneous Volterra IDE [14] with an intractable and time consuming general solution process.

Finite difference method (*FDM*), is an applicable scheme to solve coupled equations [15] and as will be mentioned in section ??, discretization of a differential equation results some ones. This method has been used to study electronic transport in nanostructures, for instance Khomyakov et. al. [16] have calculated coherent transport of a nano wire by wave functions matching in the boundary zones connecting electrodes and the scattering region using *FDM*.

In this article, using *FDM*, a simple formalism is proposed to solve equation (1.4). In this approach, derivative and integrator operators are defined then equation (1.4) is rewritten in matrix form in the presence of adequate boundary conditions (section ??).

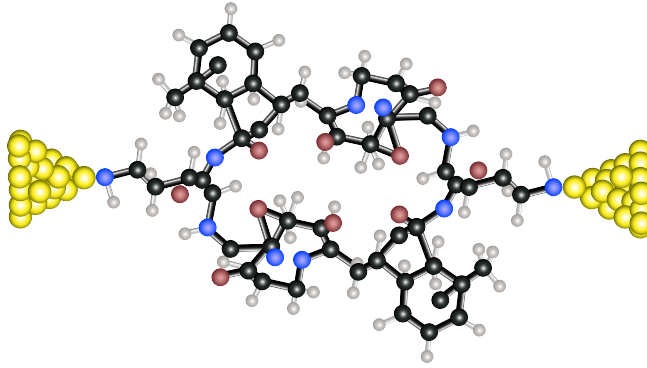


Figure 1: (Color online) A schematic figure of a metal-molecule-metal system.

In section ?? this approach is applied to calculate the Green's function, $G(t)$ for an infinite 1D chain. Results are calculated in both time-independent and time-dependent Hamiltonian cases and are compared with their analytical solutions. Beside some numerical comparisons are made between computational errors of our formalism and Dyson series and *RK* methods. Finally, this method is used to calculate the charge current in a system composed of a trans-polyacetylene molecule connected to two semi infinite 1D metal electrodes.

2 Method

2.1 Construction of the Finite Difference Scheme to solve the Volterra IDE

To solve equation (1.4) generally, consider following Volterra IDE:

$$\frac{d}{dt}y(t) = f(t)y(t) + \int_0^t k(t-\tau)y(\tau)d\tau \quad (2.1)$$

In which $y(t)$ and $f(t)$ stand for functions of an arbitrary real parameter t and $k(t-\tau)$ represents a convolution between τ and t . In order to perform numerical calculations it is really lucrative to make a discretization scheme for this IDE which allow us to use *FDM*. The grid used for discretization is a set of points $\{1, 2, \dots, n_t\}$ where n_t is an integer and shows the number of mesh points in the t domain which may be determined properly based on the fluctuations of the functions. Commonly, y_t , f_t and k_t are n_t dimensional vectors which contain all information of functions $y(t)$, $f(t)$ and $k(t)$, respectively. Beside we need two operators; a first order derivative operator and an integrator one; which are represented by $D_{n_t \times n_t}^{n_s}$ and $I_{n_t \times n_t}^{n_s}$, respectively. n_s returns to n_s -point stencil of a point in the grid in *FDM* formalism; the point itself together with its $n_s - 1$ neighbours. Clearly n_s must usually choose in such a way that be less than or equal to n_t , ($n_s \leq n_t$). Here we try to introduce these two operators properly.

The first derivative of a function $y(t)$ respect to the parameter t at a point t_i is usually approximated using a n_s -point stencil as [17]:

$$y'(t_i) \approx d_{i,i}y(t_i) + \sum_{i_s \in neighbors} d_{i,i_s}y(t_{i_s}) \quad (2.2)$$

The coefficients $d_{i,j}$ of this equation, while i and j can be integer numbers in this set $\{1, 2, \dots, n_t\}$, are well known as Lagrange interpolation coefficients [18] and are used widely in *FDM*. These coefficients should be exploited to derive $D_{n_t \times n_t}^{n_s}$ as a matrix whose elements are zero except those that are $d_{i,j}$. Up to this precision, it is straightforward to define the inverse of this derivative operator as an adequate integrator operator, namely $I_{n_t \times n_t}^{n_s}$. Uniqueness of this integrator operator imposes a boundary condition. Keeping in mind the proper initial value condition, which is $\int_0^0 y(t)dt = 0$, we pursue common procedure in the *FDM*. For each boundary condition a row and a column are added to

integrator matrix [15] so that the final integrator operator with boundary conditions is introduced as:

$$I_{(n_t+1) \times (n_t+1)}^{n_s} = \begin{pmatrix} D_{n_t \times n_t}^{n_s} & B_{n_t \times 1} \\ B_{n_t \times 1}^\dagger & 0 \end{pmatrix}^{-1} \quad (2.3)$$

In which, the elements of the matrix $B_{n_t \times 1}$ are defined as:

$$B_{t,1} = \delta_{t,1} \quad (2.4)$$

In which $\delta_{t,1}$ represents the Kronecker delta function. After inversion, we omit added row and column of integrator operator with boundary conditions, $I_{(n_t+1) \times (n_t+1)}^{n_s}$, and reshape it to new one, namely $I_{n_t \times n_t}^{n_s}$ which is integrator operator without boundary conditions. In addition to bringing forward these two operators, we need to shed light on the right hand side of the equation (2.1) and its meaning in our method. For the first part we propose a new operator which multiplies $y(t)$ by $f(t)$ and represent it with $M_{n_t \times n_t}$. Clearly it must multiply the same elements of y_t by f_t . It is satisfied by Exploiting the Kronecker delta function as follows:

$$M_{t,t'} = f_{t'} \delta_{t,t'} \quad (2.5)$$

In the second part, we must integrate a function which is multiplication of the convolution function $k(t-\tau)$ by $y(\tau)$. Hiring the predefined integrator operator and representing a new integrator operator with convolution factor by $J_{n_t \times n_t}^{n_s}$, we sufficiently introduce a matrix whose elements are defined as follow:

$$J_{t,t'}^{n_s} = k_{t-t'+1} I_{t,t'}^{n_s} \quad (2.6)$$

In which t and t' go from 1 to n_s . We can rewrite equation (2.1) in matrix form using the operators $D_{n_t \times n_t}^{n_s}$, $M_{n_t \times n_t}$ and $J_{n_t \times n_t}^{n_s}$:

$$(D^{n_s} - M - J^{n_s}) \cdot y = 0 \quad (2.7)$$

Where in it subscripts are omitted for abbreviation and matrices are multiplied in usual matrix product law.

2.2 Construction of the Matrix Finite Difference Scheme to solve MIDE

To extend our method over matrix domain, retaining their definitions, we replace the functions y , f and k with $Y_{n \times n}$, $F_{n \times n}$ and $K_{n \times n}$, respectively where n is the dimension of these matrices. The *IDE* substitutes by its matrix counterpart *MIDE* as follows:

$$\frac{d}{dt} Y_{n \times n}(t) = F_{n \times n}(t) Y_{n \times n}(t) + \int_0^t K_{n \times n}(t-\tau) Y_{n \times n}(\tau) d\tau \quad (2.8)$$

All of the matrices are time dependent. Discretization of these matrices in t domain evenuates 3D array version of them, namely $Y_{x,x',t}$, $F_{x,x',t}$ and $K_{x,x',t}$ where x , x' and t are

integer numbers. x and x' belong to set $\{1, 2, \dots, n\}$ and t goes from 1 to n_t as pointed before. Supporting matrix representation, we reshape $Y_{x,x',t}$ to $Y_{\xi,x'}$, in which ξ sweeps both parameters x and t . Consequently it becomes a $(n_t.n) \times (n)$ matrix. For consistency ξ is defined as:

$$\xi(t, x) = t + (x - 1)n_t \quad (2.9)$$

By means of our previous definitions, we construct a new first order derivative and an integrator operator in this scope. Let $\mathfrak{D}_{(n_t.n) \times (n_t.n)}^{n,n_s}$ denotes the first order derivative operator whose elements are defined as:

$$\mathfrak{D}_{\xi(t,x), \xi'(t',x')}^{n,n_s} = \delta_{x,x'} D_{t,t'}^{n_s} \quad (2.10)$$

Where $D_{t,t'}^{n_s}$ is the related matrix entry of $D_{n_t \times n_t}^{n_s}$ which was formerly defined in equation (2.2) and $\delta_{x,x'}$ is the Kronecker delta function. Suppose $\mathfrak{J}_{(n_t.n) \times (n_t.n)}^{n,n_s}$ stands for the integrator operator. The elements of this operator are determined as:

$$\mathfrak{J}_{\xi(t,x), \xi'(t',x')}^{n,n_s} = K_{x,x',t-t'+1} I_{t,t'}^{n_s} \quad (2.11)$$

In this equation $I_{t,t'}^{n_s}$ represents the proper entry of $I_{n_t \times n_t}^{n_s}$, once was defined in equation (2.3). Pursuing our procedure we need an adequate operator to multiply $F_{x,x',t'}$ by $Y_{\xi,x'}$. Let $\mathfrak{M}_{(n_t.n) \times (n_t.n)}$ represents it. Exerting the Kronecker delta function its elements are assigned as:

$$\mathfrak{M}_{\xi(t,x), \xi'(t',x')} = F_{x,x',t'} \delta_{t,t'} \quad (2.12)$$

We put equations (2.10), (2.11) and (2.12) in to the equation (2.8) to achieve its *FDM* counterpart as:

$$(\mathfrak{D}^{n,n_s} - \mathfrak{M} - \mathfrak{J}^{n,n_s}) Y_{(n_t.n) \times (n)} = \mathbf{0}_{(n_t.n) \times (n)} \quad (2.13)$$

In which $\mathbf{0}_{(n_t.n) \times (n)}$ denotes a zero matrix. Generally $Y(t)$ at $t=0$ is $Y(t=0) = Y_1$, i.e.: the Y_1 is an arbitrary $n \times n$ matrix at $t=0$ with adequate conditions based on our problem. Finally, we obtained first order linear partial integro-differential equation as a system of linear equations. To digest we get $\mathfrak{A} = \mathfrak{D}^{n,n_s} - \mathfrak{J}^{n,n_s} - \mathfrak{M}$.

$$\begin{pmatrix} \mathfrak{A}_{(n_t.n) \times (n_t.t)} & B_{(n_t.n) \times n} \\ B_{(n_t.n) \times n}^\dagger & \mathbf{0}_{n \times n} \end{pmatrix} \begin{pmatrix} Y_{(n_t.n) \times n} \\ X_{n \times n} \end{pmatrix} = \begin{pmatrix} \mathbf{0}_{(n_t.n) \times n} \\ Y_{1n \times n} \end{pmatrix} \quad (2.14)$$

Where B imposes boundary condition at $t=0$ by following definition:

$$B_{\xi(x,t), x'} = \delta_{x,x'} \delta_{t,1} \quad (2.15)$$

In which $\delta_{x,x'}$ and $\delta_{t,1}$ are the Kronecker delta function. It should be noted that X is the discarded part of the answer after solving the equation (2.14). The remainder of this paper is reserved for material to exploit the above method.

3 Numerical results

3.1 Studying the electronic transport of a one dimensional system

We start with a simple toy model. As a primarily system consider a simple *MMM* consists of two-atom molecule connected to two semi infinite 1D leads. As a primarily system, consider an infinite one dimensional chain of atoms which some part of it may counts as center part and its two tails as two semi infinite 1D electrodes (see figure 2). In

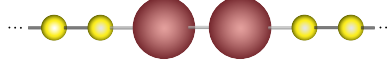


Figure 2: (Color online) Schematic illustration of a simple *MMM* consists of two-atom molecule connected to two semi infinite 1D leads.

the tight-binding approximation and second quantization representation, Hamiltonian for the molecule can be written as follows:

$$H(t) = \sum_x \epsilon_0 c_x^\dagger c_x + \sum'_{\langle x, x' \rangle} t_{x, x'}(t) c_x^\dagger c_{x'} \quad (3.1)$$

where the summations run over the lattice sites, ϵ_0 is the energy of the electrons at site x , $t_{x, x'}$ is the transfer energy between site x and x' , and c_x^\dagger ($c_{x'}$) is the creation (annihilation) operator of electrons at site x (x'). The prime on summation symbol omits the cases $x = x'$. $\Sigma(t)$ should be determined to solve equation (1.4). In this method, $\Sigma(t)$ accounts for the “interaction” of an open system; namely the center part; with the attached two ideal semi infinite leads. So the non-vanishing elements of the self-energy matrix (for this considered system, the first and the last elements) will be the conventional self-energy of an ideal semi infinite 1D chain which in the energy representation can be written as [19]:

$$\Sigma(\epsilon) = \begin{cases} \frac{v^2}{2} [V - \epsilon - i\sqrt{4 - (\epsilon - V)^2}] & |\epsilon - V| < 2 \\ \frac{v^2}{2} [V - \epsilon + \frac{(\epsilon - V)}{|\epsilon - V|} \sqrt{(\epsilon - V)^2 - 4}] & |\epsilon - V| > 2 \end{cases} \quad (3.2)$$

In which V is the bias voltage, v is the coupling energy between leads and the central molecule and ϵ is the energy. $\Sigma(t)$ will be obtained by the Fourier transform of the $\Sigma(\epsilon)$:

$$\Sigma(t) = -iv^2 \Theta(t) \frac{J_1(2t)}{t} e^{iVt} \quad (3.3)$$

where $\Theta(t)$ is the Heaviside function, J_1 is the Bessel function of the first kind and other parameters are similar to their Fourier transforms.

Rewriting the *MIDE* form of the equation (1.4) for this system, it will be found:

$$i\hbar \frac{d}{dt} G(t) - \begin{pmatrix} \epsilon_0 & t_{1,2}(t) \\ t_{2,1}(t) & \epsilon_0 \end{pmatrix} G(t) - \int_0^t \begin{pmatrix} \Sigma(t-\tau) & 0 \\ 0 & \Sigma(t-\tau) \end{pmatrix} G(\tau) d\tau = I\delta(t) \quad (3.4)$$

Instead of the Green's function, we continue our approach with time evolution operator $U(t)$ which has a simple relation with $G(t)$: $[G(t) = -i\Theta(t)U(t)]$. The boundary condition for $U(t)$ at $t=0$ is $U(0) = \hat{1}_{2 \times 2}$. Finally, to use the *FDM* for equation (3.4), some substitutions by replacing Y and Y_1 in equation (2.14) with U and $\hat{1}_{2 \times 2}$, respectively and turning K and F in equations (2.11) and (2.12) to self-energy and Hamiltonian matrices. For numerical calculations, except for mentioned cases, parameters $n_s = 11$ and $n_t = 1000$ are fixed to obtain time evolution operator (TEO) in the certain domain of t ; ($t = [0, \dots, 50]$ in this work)

Two major cases are distinguished, a MMM system in the limit of very weak electrodes coupling (isolated molecule), which means no convolution term in equation (3.4) [$v=0$ in equations (3.2) and (3.3)] and a traditional MMM system [non-zero convolution term in equation (3.4)]. The simplest model may consist of two atoms as the central molecule in which the on-site energy of the electrons ignored and the hopping terms are constant [$\epsilon_0=0$ and $t_{x,x'}(t)=1.0$ in the equation (3.1)]. For the isolated system, the exact analytical solution of the equation (3.4) for $U(t)$ can straightforwardly be found as:

$$U(t) = e^{-iHt} = \begin{pmatrix} \cos(t) & -i\sin(t) \\ -i\sin(t) & \cos(t) \end{pmatrix} \quad (3.5)$$

In this case the *FDM* solutions for real and imaginary parts of $U(t)$ are shown in figures 3 (a) and (b), respectively where in them $U_{i,j}$ stands for the i^{th} and j^{th} entry of $U(t)$ matrix. Clearly *FDM* results for elements of $U(t)$ matrix are in excellent agreement with ones which obtained from analytical solutions.

The presence of a periodic time dependent perpendicular electric field, makes a time commutative time dependent Hamiltonian with dynamic on-site energies [$\epsilon_0(t)=\cos(t)$]. Again, The exact analytical solution of the equation (3.4) for $U(t)$ in this case may be calculated as:

$$U(t) = e^{-i\int_0^t H(\tau) d\tau} = e^{-i\sin(t)} \begin{pmatrix} \cos(t) & -i\sin(t) \\ -i\sin(t) & \cos(t) \end{pmatrix} \quad (3.6)$$

The *FDM* solutions for real and imaginary parts of $U(t)$ are shown in figures 3 (c) and (d). Once more, analytical results are consistent with *FDM* answers for elements of $U(t)$ matrix superbly.

In the case of time dependent, non-commutative Hamiltonian in time, a simple case with vanishing on-site energies; $\epsilon_0(t)=0$ and time dependent phase hopping $t_{x,x'}(t) =$

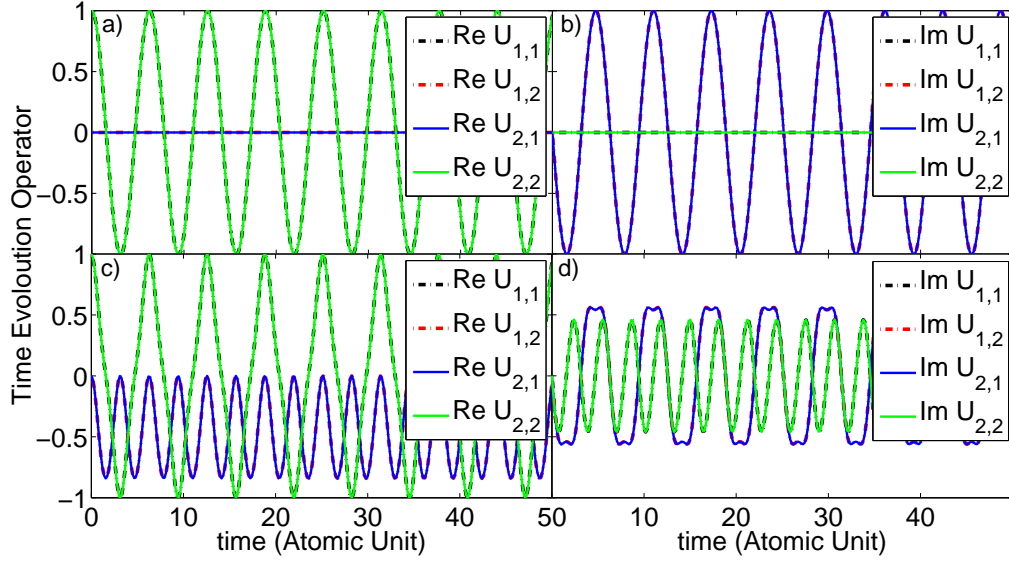


Figure 3: Real (a and c), and imaginary (b and d), parts of TEO elements for an isolated system, in the cases of time independent (a and b) and a time commutative time dependent (c and d) Hamiltonians, as mentioned in equations (3.5) and (3.6), respectively.

$e^{-i\Phi(t)}$ are studied. This phase hopping may emerge from an external magnetic field or strain, *etc* [20]. Regardless of the physical source of this phase, to facilitate the calculation, a simple time dependent function $\Phi(t) = \Omega t$ with $\Omega = 1.0$ is selected. Dyson series are usual method to study this types of Hamiltonian [21] which in compact form, exploiting time order operator T_τ to respect the time order, it can be noted as [22]:

$$U(t) = T_\tau(e^{-i\int_0^t H(\tau)d\tau}) \quad (3.7)$$

Although this equation is not as tractable as its former counterparts, it can be solved analytically for this specific Hamiltonian and so its answer will be found as:

$$U(t) = \begin{pmatrix} A(t) & C(t) \\ -C^*(t) & A^*(t) \end{pmatrix} \quad (3.8)$$

$$A(t) = \frac{1}{10}[(5 - \sqrt{5})e^{-i\frac{\sqrt{5}+1}{2}t} + (5 + \sqrt{5})e^{i\frac{\sqrt{5}-1}{2}t}]$$

$$C(t) = -\frac{2i}{\sqrt{5}}e^{i\frac{t}{2}}\sin(\frac{\sqrt{5}t}{2})$$

Using *FDM*, numerical solution of the equation (3.7) for this specific Hamiltonian even-tuated to figures 4 (a) and (b) for real and imaginary parts of the elements of TEO $U(t)$.

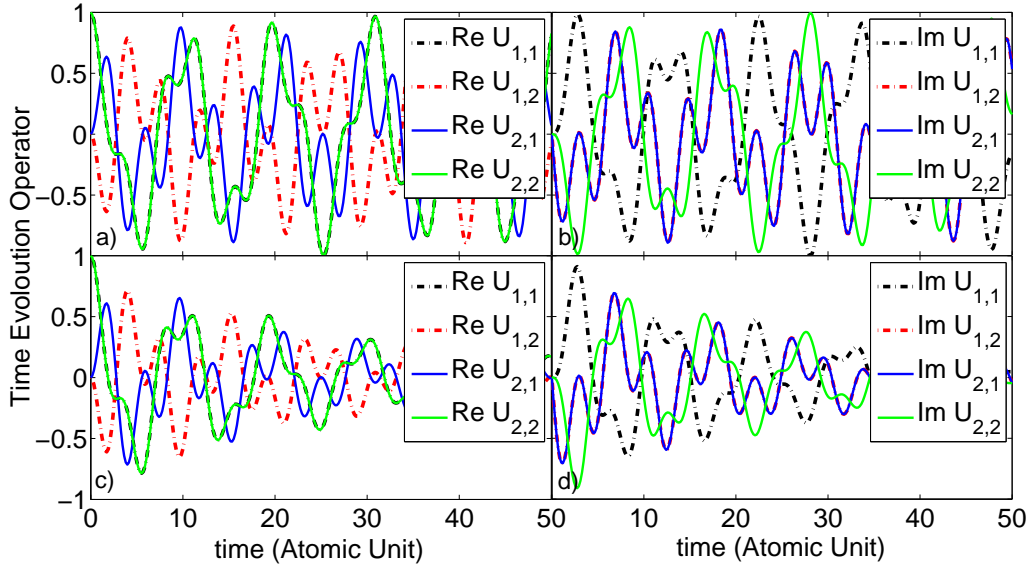


Figure 4: Real (a and c), and imaginary (b and d), parts of TEO elements for an isolated (a and b) and an interacting (c and d) systems, in the case of time dependent non-commutative Hamiltonian in time, as mentioned in equations (3.7) and (3.4), respectively.

In all three types of systems the elements of the TEO are not only periodic in time but also non-dissipative which the later one is a natural property of an isolated system. This may be counted as a good evidence for authenticity of the procedure.

For an “interacting” system which is more interesting, equation (1.4) contains the convolution term. A simple model may be constructed with vanishing on-site energies; $\epsilon_0(t)=0$ and time dependent hopping $t_{x,x'}(t)=e^{-i\Phi(t)}$ with $\Phi(t)=\Omega t$ for central molecule and a weak coupling probability between molecule and electrodes; $v=0.2$ (as described in third former isolated system). Unfortunately analytical solution for this system is intractable but its numerical solution using *FDM* led to calculate real and imaginary parts of $U(t)$ (figures 4 (c) and (d), respectively).

Dissipative behaviour of elements of the TEO may be regarded as a good physical proof for “interacting” nature of the system.

To illustrate both advantages and deficiencies of the *FDM*, comparison of it with Dyson series method and *RK* family methods is appropriate. Figure 5 (a) shows the error estimates for four distinct conditions for a short period of time after its initial condition $t_0=0$. In an isolated system “without any interactions with electrode”; i.e. [$v=0$ in equations (3.2) and (3.3)]; the *IDE* equation (1.4) is modified to a trivial partial differential equation(*PDE*) so *RK* family methods may be the best choice to solve it since *RK* family methods are faster and more accurate than other ones [dashed line in figure 5 (a)]. Turning the “interactions” on, a general Volterra *IDE* [equation (1.4)] must be solved. Because

the *RK* method is a very rough approximation to calculate an integral, this method deviates rapidly [dashed dot line in figure 5 (a)]. Power series characteristic of Dyson series method in time causes it to fluctuate in time faster than *FDM*. Comparison of dot line which stands for Dyson series method with solid line which represents the *FDM* diagrams in figure 5 (a) can clarify it. Therefore in the vicinity of initial condition in time, both Dyson series method and *FDM* are applicable but the former one is more accurate. After a long enough period of time, effect of the higher power of time in Dyson series causes larger fluctuations and more deviations in its solution and only *FDM* can be tractable and accurate. All of them are illustrated in figure 5 (b).

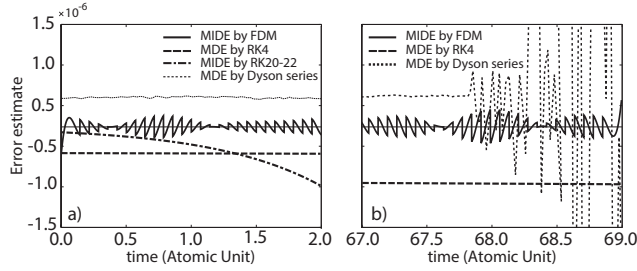


Figure 5: Error estimate of different methods related to a short period a) and a long enough period b) of time.

3.2 FDM application to study electronic transport in a trans-polyacetylene molecule

Investigating charge transport in molecular junctions has been interesting for scientists [1, 23–26]. Electrical transport properties of a system have a closed relation to the time evolution of the charge density in it. Consider a MMM system composed of a trans-polyacetylene molecule which contains 20 atoms as the central molecule and two 1D ideal semi infinite electrodes (figure 6), beside the assumption that the coupling energy between the polyacetylene molecule and each electrode is $v = 0.5$ and an electric potential difference is applied between leads $\Delta V = 2\text{volt}$; the self-energy of each electrode can be calculated by equation (3.3) in the time representation. Hamiltonian of the trans-polyacetylene was written in the tight binding approximation and second quantization representation [27, 28] as below:

$$H = \sum_x \epsilon_0 c_x^\dagger c_x + \sum_{\langle x, x' \rangle} t_{x, x'} c_x^\dagger c_{x'} \quad (3.9)$$

$$t_{x, x'} = t_0 - 2\alpha(-1)^{\min(x, x')} u_0$$

In which the summations run over the lattice sites and the on-site energy of electrons (ϵ_0) is set properly. The hopping terms $t_{x, x'}$ relate to nearest neighbour sites. There are three empirical parameters which clarify the magnitude of the hopping integrals. The

carbon-carbon atoms hopping integral related to π orbitals equals to $t_0 = 2.5\text{eV}$. The electron-phonon coupling constant is $\alpha = 4.1\text{eV}\text{\AA}^{-1}$ and $u_0 = 0.04\text{\AA}$ represents the constant displacement due to Peierls distortion because of dimerization [20, 28]. Applying this Hamiltonian and using the *FDM*, the equation (1.4) can be solved numerically. Suppose

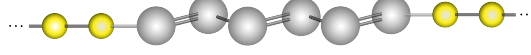


Figure 6: (Color online) A sketch of the polyacetylene molecule between two semi infinite 1D electrodes.

$|\psi_i, t=0\rangle$ represents a state that an electron exists on i th atom (in the local atomic state i) at the time $t=0$. The TEO traces this state in the next time t as follow:

$$|\psi_i, t\rangle = U(t) |\psi_i, t=0\rangle \quad (3.10)$$

then the probability density of transition from i th atom at time $t=0$ to j th atom at time t is straightforward as:

$$P_{i,j} = |\langle \psi_j, t | \psi_i, t=0 \rangle|^2 \quad (3.11)$$

Evolution of this probability density in time may interpret as the movement of an electron wave packet between different atomic states in the system. For instance figure 7 shows the evolution of transition probability density from the first atomic state, $i=1$ at time $t=0$ to all other states at any time (equation (3.11)).

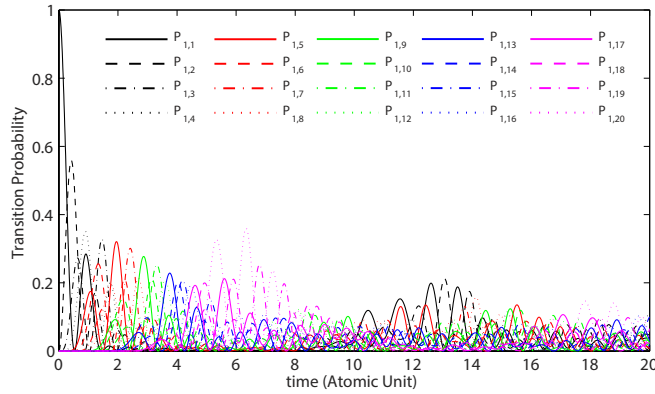


Figure 7: (Color online) Transition probability from the first atomic state at time $t=0$ to other states at time t .

To study charge transport in the system one needs to define the charge density in it. Assume $q_i(t)$ denotes the charge density of the atomic state i at time t , which is related to initial charges on all states, $q_j(0)$ as:

$$q_i(t) = \sum_j q_j(0) |\langle \psi_i, t | \psi_j, t=0 \rangle|^2 \quad (3.12)$$

while its discrete counterpart can be rewritten in the matrix representation as:

$$\mathbf{q}^\psi(t) = \mathbf{P}^\psi(t) \mathbf{q}^\psi(0) \quad (3.13)$$

In which \mathbf{P}^ψ represents the matrix of the transition probabilities between atomic states and \mathbf{q}^ψ is a vector containing the charge of each one. Applying the TEO on the charge density one may find the propagation of it in the system during a specific time. For instance assume, at the initial time ($t = 0$) one electron is arrived in first atom of the molecule from left lead ($q_i(0) = \delta_{i,1}$). The snapshots of the $\mathbf{q}^\psi(t)$ at different times are shown in figure 8. At the time $t = 5.5$ (*Atomic Unit*) this electron wave packet collides to the right lead and diffracts [see the figure 8(d)]. Some parts of it reflected back and others transferred to the right lead and this process persists in time. The time evolution of the Hamiltonian eigenstates is useful. Assume $|\epsilon\rangle$ denotes the eigenstate with eigenvalue ϵ . This means that initially the equation (3.14) holds for this state so $|\epsilon, t=0\rangle$ is calculated by:

$$H(0)|\epsilon, t=0\rangle = \epsilon|\epsilon, t=0\rangle \quad (3.14)$$

then its time evolution can be calculated by:

$$|\epsilon, t\rangle = U(t)|\epsilon, t=0\rangle \quad (3.15)$$

Suppose $q_\epsilon(t)$ denotes the charge density in energy level ϵ at time t . Rewriting equations (3.12) and (3.13) in these new basis, one may found:

$$q_\epsilon(t) = \sum_{\epsilon'} q_{\epsilon'}(0) |\langle \epsilon, t | \psi_{\epsilon'}, t=0 \rangle|^2 \quad (3.16)$$

and its discrete representation as:

$$\mathbf{q}^\epsilon(t) = \mathbf{P}^\epsilon(t) \mathbf{q}^\epsilon(0) \quad (3.17)$$

In which \mathbf{P}^ϵ is a matrix which represents transition probabilities between energy eigenstates and \mathbf{q}^ϵ denotes a vector contains the charge of these energy levels. Consider half filling situation with sorted states as initial state at the time $t=0$ and define the Fermi energy at the middle of the energy difference between highest full state and lowest empty one, $E_F = 0.5eV$. The snapshots of the time evolution of this initial state were shown in Figure 9 in several times. During this process, states whose their energy are near the Fermi energy, lose their charge while others are robust. These lost charges are transferred to the leads and make a charge current.

To calculate the current, definition of the total charge in the center part of the system at any time t is mandatory. This can be properly defined by the summation of total charge in all atoms of central molecule at any time t , as:

$$q_T(t) = \sum_i q_i(t) \quad (3.18)$$

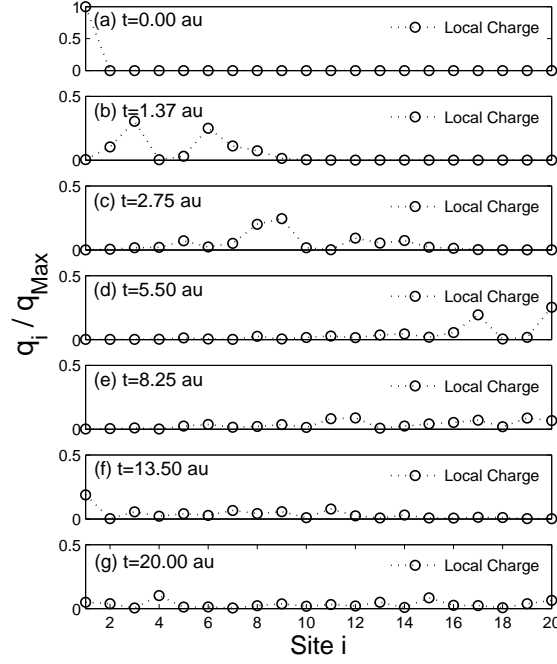


Figure 8: The evolution of a charge density from left to right snapshots in the atomic state basis.

Evolution of this total charge in time illustrates the meaning of the charge current in the molecule. Three different cases were shown in figure 10. If the molecule become separated from the leads, its total charge must be constant which is compatible with the black dashed line diagram in figure 10. The red (blue) line diagram refers to the situation in which the electron is arrived in first (last) atom from left (right) lead at time $t = 0$. Generally, amount of the charge reduces during the time evolution. At first this charge reduces rapidly and leaks to the leads but then partially increases due to contact effect. The potential difference between the leads causes the total charge magnitude for evolution from the left to the right of the molecule be grater than its reverse direction. When the maximum of the charge density collides to the next lead, these two lines are tangent to each others during the large reduction due to the charge leaking to the leads [compare the violet dot line in figure 7 with figure 10 at time $t = 5.5(AtomicUnit)$] and therefore intersect where direction of the charge flow changes (points c_1 , c_2 and c_3). The difference between the charge magnitude before and after charge leaking, determines net amount of charge transferred to the leads which makes a charge current. Comparison between this current interpretation and formal one which relates to the current density operator is beneficial $\{j(t) = \frac{\hbar}{m} \Im[\psi^\dagger(t) \nabla \psi(t)]\}$. The charge flow is plotted in figure 11. The extremums in this diagram are equal to collisions of the charge density with leads

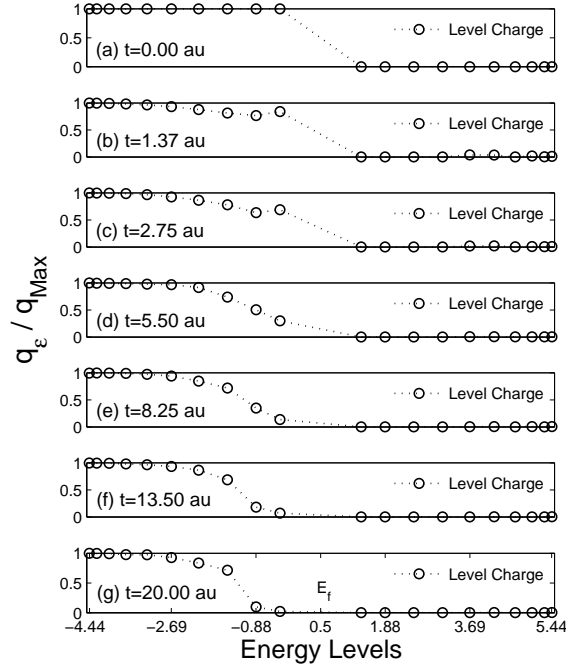


Figure 9: The evolution of a charge density from left to right snapshots in the energy basis.

which is satisfiable. Applying this method for the first and the last atoms of the molecule, we calculated the current. All the charge evolutions in these two atoms emerge from three distinct sources: 1. The initial charges which have remind there yet $q^{L(R)}(t)$, 2. The charges which depend on other sites $q^{L(R) \rightarrow R(L)}(t)$, 3. The interaction with the adjacent lead $q^{L(R) \rightarrow L(r)}(t)$. So we can find the total transferred charge from the first atom as:

$$\begin{aligned}
 q^L(t) &= P_{1,1}(t)q^L(0) \\
 q^{L \rightarrow R}(t) &= \sum_{j=2}^n P_{1,j}(t)q^L(0) \\
 q^{L \rightarrow L_l}(t) &= q^L(0) - q^L(t) - q^{L \rightarrow R}(t)
 \end{aligned} \tag{3.19}$$

and so for the last atom we have:

$$\begin{aligned}
 q^R(t) &= P_{n,n}(t)q^R(0) \\
 q^{R \rightarrow L}(t) &= \sum_{j=1}^{n-1} P_{n,j}(t)q^R(0) \\
 q^{R \rightarrow L_r}(t) &= q^R(0) - q^R(t) - q^{R \rightarrow L}(t)
 \end{aligned} \tag{3.20}$$

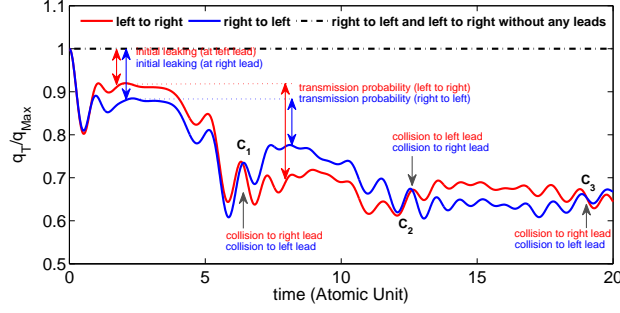


Figure 10: (Color online) The total charge in molecule.

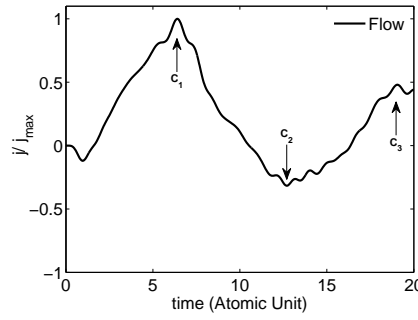


Figure 11: The charge flow which is calculated by the energy eigenstates.

then the transferred charge from the molecule at any time t is calculated as:

$$q(t) = \frac{1}{2} \{ [q^{L \rightarrow R}(t) + q^{R \rightarrow L_r}(t)] - [q^{R \rightarrow L}(t) + q^{L \rightarrow L_l}(t)] \} \quad (3.21)$$

As our computations are in the *independent electron approximation*, total transferred charge at every time t , is sum of all transferred charges in any infinitesimal time period $\delta\tau$. So we have:

$$q(t)^T = q(t) + q(t - \delta\tau) + q(t - 2\delta\tau) + \dots \simeq \int_0^t q(t - \tau) d\tau \quad (3.22)$$

Therefore its time derivation will give the current $[I(t) = \frac{d}{dt}q(t)^T]$. After a proper time, for every constant voltage an steady current I_s , will pass through the system. Figure 12 shows the current diagram at constant voltage $v = 5V$ where the steady current is $I_s = 0.96mA$. This tranquility time may interpret as a relaxation time, τ , which can be calculated by fitting the diagram of figure 12 to a proper function like $f(t) = 1 - e^{-\frac{t}{\tau}}$. The inverse of this relaxation time (τ^{-1}) may be regarded as resistivity (ρ) of this system.

Following this procedure for other voltages, we can find the voltage dependent diagrams of these three parameters. Indeed the relaxation time-voltage, the resistivity-

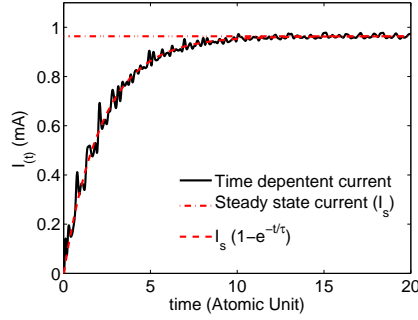


Figure 12: (Color online) The charge current as a function of time (t) in the system at a constant voltage

voltage and the current-voltage diagrams are found as depicted in figures 13 (a), (b) and (c), respectively. Existence of steps in the current-voltage diagram, is a proper evidence for quantum confinement effect.

4 Summery

In summery, we propose a new numerical method to study time evolution in physical systems by using *FDM*. To solve the correspondent *Volterra integro-differential equation*, first we introduced a first order derivative and an integrator operators and discretized them. Using this method we studied the time evolution of a 1D chain Hamiltonian in different situations and compared our results with Dyson series and Runge Kutta. Our method not only is compatible with analytical results but also is more accurate than other numerical methods. Furthermore we study the charge transport in a trans-polyacetylene chain as a central molecule of a *MMM* system by considering time evolution of its charge density and then calculated its current- voltage diagram.

The most significant application emerges from this method that has not instantly mentioned is that it can properly be applied for time dependent Hamiltonians regardless of the source of this time dependency. So it not only can be used for time dependent Hamiltonian but also may be used for time dependent self-energies related to the electrodes in *MMM* system.

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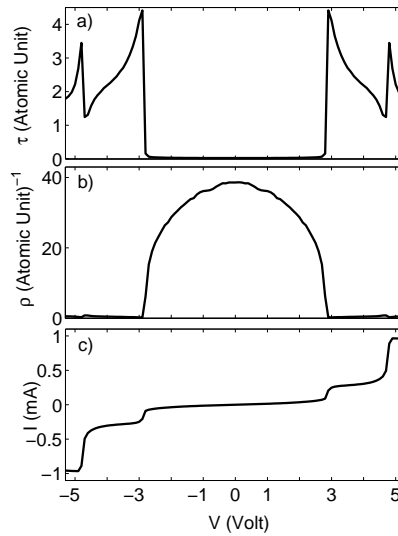


Figure 13: The relaxation time-voltage (a) the resistivity-voltage (b) and the current- voltage (c) diagrams.

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